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AUTHOR(S):

Watanabe, Akira; Tsuji, Fukuju; Ueda, Shizuo

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Study on Surface Electricity. (XIX)

On Capacity Measurement of Dropping Mercury Electrodes by Resonance Method

Akira WATANABE, Fukuju TSUJI and Shizuo UEDA*

(Tachi Laboratory)

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As the total capacitance of a dropping mercury electrode increases with the drop growth, a resonance phenomenon can be observed at a certain instant in each drop period by proper choice of a.c. frequency and load inductance. The resonance curve can be reproduced on the screen of a cathode-ray oscilloscope by using a synchronizing device. As the resonant capacitance decreases with increasing inductance at a given frequency, a point is determined where the circuit resonates at a moment just before the drop falls. From this resonant capacitance and the interfacial area, the differential capacity per unit area can be calculated easily.

The electrical double layer capacity at a mercury-electrolyte solution interface is a function of applied polarizing potential, which has been measured by various methods by the present authors as well as by various authors¹⁾. All of their experimental devices were, however, not satisfactory in their accuracy and simplicity, although recent developments in them were remarkable.

M. A. Proskurnin and A. N. Frumkin²⁾ showed in 1935 that the observed values obtained before were much reduced by the presence of traces of surface active impurities in solution, and got fairly high values by careful experimentation. Recently David C. Grahame³⁾ proved by experiment that this difficulty could be avoided if a dropping mercury cathode was used, because the adsorption rates of the small amounts of such materials were much smaller than the rate of growth of mercury drop. It is desirable, therefore, to use a dropping electrode for the precise measurement of the electrical double layer capacity.

In the preceding papers⁴⁾ we described the capacity measurement by resonance method using U-effect II. This is a very simple and accurate device save its defect in reproducibility caused by hysteresis. This defect is, of course, easily conquered by the use of a dropping cathode mentioned above. It is a simple matter now to construct a new device of capacity measurement by combining them, which shall be explained in detail here.

* 渡辺 昌, 辻 福寿, 上田 静男

1. GROWTH OF A MERCURY DROP

The non-electrical properties of a dropping mercury cathode were examined in detail by G. S. Smith in his recent paper in 1951⁶⁾. We shall consider them separately in relation to our case.

(1) Balance Equation of a Mercury Drop.

In the first approximation, the final weight of a drop (that just before it falls) is in balance with the upward force of interfacial tension round the circumference of this capillary orifice, but there is an excess force due to the curvature of the mercury drop, which reduces the upward force. Since the drop is approximately spherical, the equation of balance reads

$$\frac{W}{1000} - \frac{D-d}{D}g = 2\pi\rho r \left(1 - \frac{\rho}{R}\right), \quad (1)$$

where W is the drop weight in air (mg), D and d the densities of mercury and solution, ρ and R the radii of the capillary orifice and mercury drop (cm), and r the interfacial tension between mercury and solution (dynes/cm), respectively. In this equation the term $(2r/R)$ ($\pi\rho^2$) is the excess pressure due to the drop curvature.

It is clear that we need not consider the effect of capillary orifice in our experiment, because we used always the same capillary.

(2) Drop Weight and Interfacial Tension.

The interfacial tension is a function of applied polarizing potential (electro-capillary curve) as well as of the species and composition of solution. It must also be remembered that this quantity is decreased by the superposition of a.c.⁶⁾

Putting $D = 13.53$ and $d = 1$ at 25°C., we get from eq. (1)

$$r = \frac{0.1445 W}{\rho(1 - 38.42\rho/W)^{1/3}}, \quad (2)$$

which gives the function of drop weight in relation to the interfacial tension.

(3) Rate of Flow of Mercury During Drop Growth.

The back pressure decreases with increasing drop radius. Putting the mercury head and back pressure in h and h_b , respectively, we get

$$h - h_b = h - 2r/gDr = h - 1.508 \times 10^{-4}r/r.$$

When the constant rate of mercury flow were M when h_b were absent, and when the real drop weight is w at time t (sec) after the dropping begins, following equation is obtained

$$dw/dt = M(1 - h_b/h) = M(1 - s/w^{1/3}),$$

with

$$s = \gamma/(172.7 h).$$

In an ordinary condition $h \gg h_b$ we get

$$dw/dt \approx M/(1 + s/w^{1/3} + s^2/w^{2/3}).$$

Integrating with t , with the initial condition, $w \approx 0$ at $t = 0$, we get

$$Mt = w + 3s w^{2/3}/2 + 3 s^2 w^{1/3}.$$

Inversion of variables, with approximation of neglecting s^3 terms, yields

$$w = Mt - 1.5M^{2/3} t^{2/3} \gamma/(72.7 h) - 1.5 M^{1/3} t^{1/3} \gamma^2/(172.7 h)^2, \quad (3)$$

where the value of s is substituted.

When we take only the first term in the last equation, w is a linear function of t , and the rate of flow has a constant value depending on the mercury head. The interfacial tension effects it in the second approximation.

2. RESONANCE

We do not give detailed descriptions on resonance phenomenon and related quantities here¹⁾. As is shown in section 1 the mercury drop grows with time, increasing the interfacial double layer capacity C with it, from the start of dropping, i.e.

$$C = C_0 a, \quad (4)$$

where C_0 is the double layer (differential) capacity per unit area ($\mu F/cm^2$), and a the interfacial area (cm^2), respectively. From eq. (3) we get

$$a = k_1 t^{2/3} (1 - k_2 \gamma t^{-1/3} - k_3 \gamma^2 t^{-2/3})^{2/3}, \quad (5)$$

where k_1 , k_2 and k_3 are constant for a given capillary system.

When we connect an inductance L to the interfacial phase, which consists of equivalent condenser C and solution resistance R_0 in series⁷⁾ (Fig. 1), and feed a

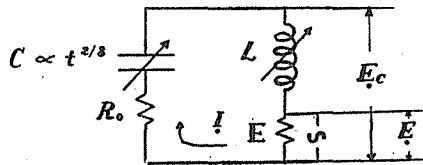


Fig. 1.

small a.c. voltage E to this circuit, the a.c. voltage between the two terminals of the interfacial phase E_c has its maximum value when

$$f = 1/(2\pi\sqrt{LC}), \quad (6)$$

where f is the frequency of a.c. (cps). (Resonance).

Q-value of this circuit is given by

$$Q = E_c^{max}/E = 1/(2\pi f \cdot C \cdot R_t),$$

where E and E_c are the effective values of E and E_c , R_t the equivalent total resistance, in which are included the interfacial absorption of Counter U-effect³⁾, solution resistance and the resistance in load circuit⁴⁾.

With proper values of L and f , the value of the double layer capacity must satisfy eq. (6) at a time $t = t_r$, from which we can calculate the value of a by eq. (5). We can, therefore, estimate the value of C_0 from eq. (4). As is clear from eq. (5), however, that the calculation of a from t_r is considerably troublesome and includes several coefficients, which must be given from other data, we used here following conventions: We measured the value of $L = L_r$ with which the circuit resonates when $t_r = T$ (the instant just before the drop falls), from which we can calculate the value of $a = A$ at $t = T$ by simple geometrical method. The value of C_0 is given easily by eq. (4). Of course, A is a function of r , as is evident from eq. (2), and we must measure W at every measurements of L_r .

Eq. (5) shows that the greater the value of t the smaller the slope of a with t (da/dt) is, and, therefore, the error in the value of L_r at $t_r = T$ is smaller than those at any other instant of t_r smaller than T .

3. EXPERIMENTAL APPARATUS

The experimental circuit is shown schematically in Fig. 2. The large mercury pool underwards in the dropping cell is the reference electrode, against which the

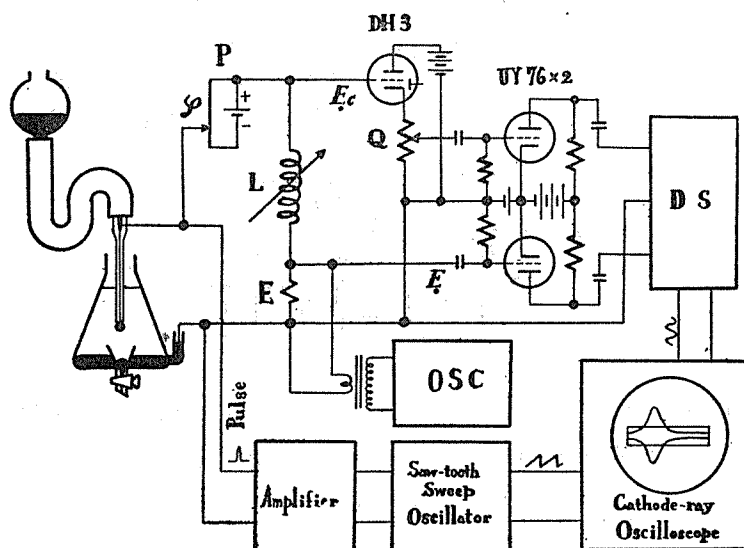


Fig. 2.

polarizing d.c. potential (ϕ) is fed to the dropping mercury cathode from a potentiometer (P). ($0 \sim -2.0$ v). The last mentioned is connected with the resonance circuit in series, decreasing Q-value, but its inner resistance is taken as low as 15 Ohms, which is negligible compared with other resistances in the circuit. L is the load inductance, which is a variable inductometer ($70 \sim 250$ mh), and whose resistance is about 100 Ohms. We feed an alternating voltage ($200 \sim 500$ cps) generated by a valve oscillator (OSC) to this circuit by means of an input resistance E , whose resistance is as small as 3 Ohms. We prevented the variation of the input alternating voltage with the change of the reactance of the resonance circuit by using a transformer coupling E and OSC with low secondary impedance. The input alternating voltage is always maintained constant (7.4 mV).

The resonant voltage E_c is fed to the grid of a cathode follower pre-amplifier tube (DH 3), which is coupled to the next tube (UY 76) by a dividing resistance Q . The input voltage E is fed to another pre-amplifier (UY 76). The outputs of these two amplifiers for E_c and E are coupled through a Dual Scoper (DS) to the vertical axis of a cathode-ray oscilloscope. As the gains of the two amplifiers are so adjusted as to give the same gains when the dividing resistance Q has its maximum resistance value, we can directly know the Q-value from the reading of Q .

A pulse voltage is generated at L when the mercury drop detaches the capillary, which is fed through an amplifier to the thyatron grid of a sweep generator. By this, we can get a saw-tooth wave sweep voltage synchronized with the mercury drop, which is fed to the horizontal axis of the cathode-ray oscilloscope.

Now, with proper values of L and f , we observe traces repeatedly at every period of drop growth on the screen of the oscilloscope, as are shown in Fig. 3a.

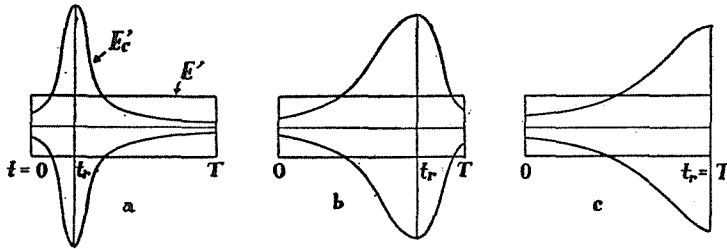


Fig. 3

The horizontal axis gives the reading of time t , and hence, implicitly the value C of the interface. E' and E_c' give the envelopes of the input (constant) voltage E and the resonant voltage E_c . The latter is the so-called resonance curve, and its maximum point indicates resonance point. When we make $E' = E_c'^{max}$ by adjusting Q , its reading Q is just the Q-value of this circuit.

It is evident from eq. (6) that with increasing L the resonating value of C decreases, and hence the position of $E_c'^{max}$ of the trace drifts to the right (that is,

to the position of increasing t) as is shown in Fig. 3b, and we can ultimately determine the value of L_r where $E_c'^{max}$ is at $t_r = T$. (Fig. 3c). Beyond this, the circuit does not resonates any more.

For the calculation of C_0 , we must calculate C which satisfies eq. (6) with the value of L_r at T (case c above) and that of A . The latter quantity is easy to get for spherical drops. The former, however, suffers from various errors due to several approximations in obtaining eq. (6), and especially so with the circuit of low Q -values. We, therefore, used a substitution method by connecting a standard variable condenser and a resistance box in series in place of the cell and observed their readings which gave the same L_r and Q as the cell.

4. RESULTS

We measured the differential double layer capacities at polarizing potentials between 0 and -2.0 V with various salt solutions. Here we only show in Table 1 the figures obtained by 1 N. KCl aq. The electrocapillary maximum potential was

Table 1.

Differential double layer capacity at Hg-N.KCl aq. interface.

$W \approx 8 \sim 11$ mg

$T \approx 1 \sim 2$ sec

$E = 7.4$ mV

$\varphi_{max} = -0.54$ V

φ (V)	f (cps)	L (mh)	C (μ F)	A (cm ²)	$C_0 = C/A$ (μ F/cm ²)
-0.15	200	169.5	3.555	0.03852	92.29
-0.2	300	97	2.825	3942	71.68
-0.3	300	143.5	1.838	4045	45.45
-0.35	300	146	1.800	4092	43.98
-0.4	300	126	2.107	4110	51.27
-0.45	300	125	2.130	4110	51.83
-0.5	300	132	2.003	4159	48.17
-0.6	300	167.5	1.580	4159	37.99
-0.7	400	123	1.225	4092	29.94
-0.8	400	178.5	0.847	4092	20.70
-0.9	400	206	0.730	4026	18.13
-1.0	500	131	0.730	3960	18.43
-1.1	500	141	0.678	3870	17.52
-1.2	500	143.5	0.666	3765	17.69
-1.3	500	143.5	0.666	3660	18.03
-1.4	500	149	0.640	3526	18.15
-1.5	500	150	0.638	3384	18.85
-1.6	500	142.5	0.671	3215	20.87
-1.7	500	142.5	0.671	3037	22.15
-1.8	500	151.5	0.630	2865	21.99
-1.9	500	116	0.825	2678	30.80

determined by a surface tension measurement to be $\varphi_{max} = -0.54$ V. The capacities per unit area are plotted against $\varphi - \varphi_{max}$ in Fig. 4. The shape and position

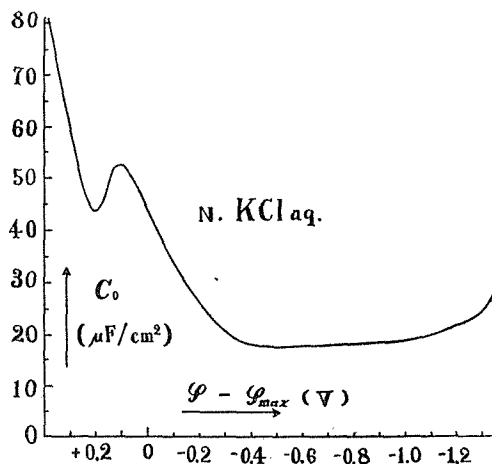


Fig 4.

of the curve is in good agreement with other authors' results⁹⁾, showing a hump near surface charge zero potential (φ_{max}) and giving flat minimum of about 18 $\mu\text{F}/\text{cm}^2$ at cathodic branch.

5. CONCLUSION

Many results were obtained by this method, among which only those of mercury-1 M KCl aq. interface are given in this paper. The results were very satisfactory, the error of C_0 being only $\pm 0.2 \mu\text{F}/\text{cm}^2$. Various interesting features were discovered by these measurements, all of which must, however, be postponed until next paper because of the limited space.

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